

A STUDY OF POLYMERS  
CONTAINING SILICON-NITROGEN BONDS

Progress Report for the Period  
May 4, 1963 to June 3, 1963

To

GEORGE C. MARSHALL SPACE FLIGHT CENTER  
National Aeronautics and Space Administration  
Huntsville, Alabama

Project 1259, Report 28

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Contract NAS 8-1510

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June 14, 1963  
5948-1259-XXVIII

CR-50,136

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## ABSTRACT

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The investigation of trimethylsilyl derivatives of hexaphenylcyclotrisilazane as starting materials for polymers was continued. N, N'-bis(trimethylsilyl)hexaphenylcyclotrisilazane polymerized in 23 hours at 400°C to form a polymer that had good thermal stability. In a brief examination, nothing was found to indicate that it was superior to the polymer made from N-trimethylsilylhexaphenylcyclotrisilazane. Preparation of the bis compound proved to be considerably more difficult than preparation of the monosilyl derivative. Potassium did not react with hexamethylcyclotrisilazane unless styrene was added, which showed that the acidity of hexamethylcyclotrisilazane is appreciably less than that of hexaphenylcyclotrisilazane.

A polymeric compound containing Si-N units bridged by phenylene units was prepared. Its molecular weight was not high, and it evidently contained some oxygen, but it could be polymerized further to form a fairly tough film with excellent thermal stability. Further improvement is needed in the method of synthesis to obtain the pure 1,4-bis(diphenylchlorosilyl)benzene starting material for polymerization.

# A STUDY OF POLYMERS CONTAINING SILICON-NITROGEN BONDS

## I. INTRODUCTION

New types of silicon-nitrogen compounds are being studied with the object of producing thermally stable materials that will be useful in the space program. Previous results have shown that silicon-nitrogen compounds rank high in thermal stability as compared with any organic compounds and that they are capable of being prepared with wide variations in physical properties. The outstanding problem has been to produce polymers with high enough molecular weights to have good strength characteristics. Previous work has disclosed a great deal about properties and methods of synthesis, and this information is now being extended. This report covers the second month of the fourth year of the project.

The potassium derivatives of cyclic silazanes are being investigated as intermediates in the synthesis of polymers and derivatives with special properties. Potassium reacted readily with hexaphenylcyclotrisilazane and the potassium derivative proved to be a convenient route to the mono-trimethylsilyl derivative. However, it was far more difficult to attach the second trimethylsilyl group to the hexaphenylcyclotrisilazane. Both the mono- and bis(trimethylsilyl) derivatives polymerized without foaming at 400°C. Study of this reaction is being continued in the effort to produce a useful polymer with high thermal stability.

Potassium did not react with hexamethylcyclotrisilazane unless styrene was added. With styrene, it reacted quickly, and the product was silylated to produce N-trimethylsilylhexamethylcyclotrisilazane for future work on polymerization.

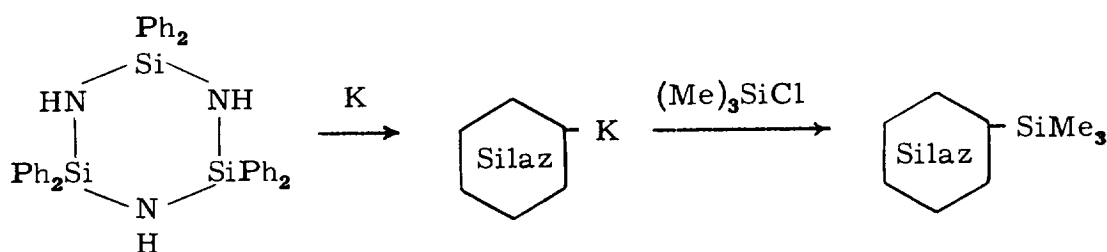
A silicon-nitrogen polymer with phenylene bridges between Si-N-Si groups was prepared, but it evidently contained an appreciable amount of oxygen. Consequently, although some of its thermal properties were encouraging, it will have to be made in a purer state for the data to be significant.

## II. POLYMERIZATION OF SILYL DERIVATIVE OF CYCLIC SILAZANES

### A. Discussion

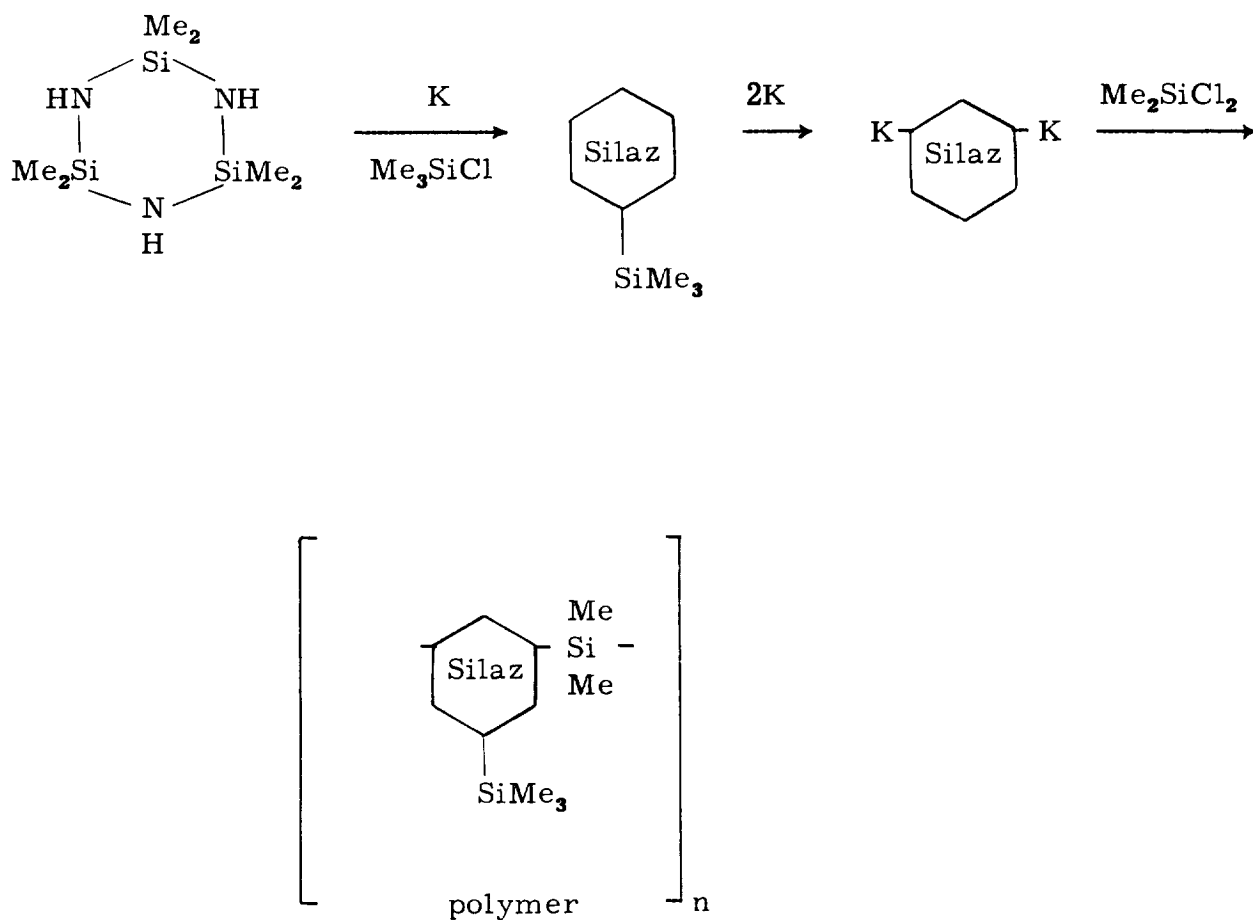
The N-trimethylsilyl derivatives of cyclic silazanes are being investigated to determine whether they can be used to make polymers with good thermal stability and other desirable properties. The preceding report described the thermal polymerization of N-trimethylsilylhexaphenylcyclotrisilazane by heating at 400-450°C to form a black, benzene-soluble polymer that softened only when heated above 450°C. In the past month, a similar material was formed by heating N,N'-bis(trimethylsilyl)hexaphenylcyclotrisilazane at 400°C. The preparation of the bis derivative proved to be difficult, because of the difficulty of making the second substitution. The first trimethylsilyl group was attached to the hexaphenylcyclotrisilazane ring relatively easily, but attempts to attach the second led to mixtures that were difficult to separate. Polymerization of the monosilyl substituted hexaphenylcyclotrisilazane will be studied in more detail to determine whether the reaction proceeds by a mechanism similar to the polymerization of hexaphenylcyclotrisilazane.

Potassium proved to be useful in the preparation of derivatives of hexaphenylcyclotrisilazane;



but it did not react as readily with hexamethylcyclotrisilazane. Evidently the methyl groups on the silazane ring do not make the N-H groups sufficiently acidic for reaction with potassium. However, the addition of styrene caused the metalation of the ring to proceed satisfactorily. The

use of styrene was suggested by Breed<sup>1</sup> and Goubeau.<sup>2</sup> The trimethylsilyl-hexamethylcyclotrisilazane is desired for future studies of polymerization by the following reactions:



1. L. W. Breed, R. L. Elliott, Quarterly Report 4, Army Project 593-32-002, Contract DA-23-072-ORD-1687, 15 October 1962.
2. V. J. Goubeau and J. Jimenez-Barbera, Z. anorg. allgem. Chemie **303**, 217-226 (1960).

B. Experimental Details

1. N,N'-bis(trimethylsilyl)hexaphenylcyclotrisilazane

Attempts were made to prepare N,N'-bis(trimethylsilyl)hexaphenylcyclotrisilazane both by monosilylation of N-trimethylsilylhexaphenylcyclotrisilazane and by bis-silylation of hexaphenylcyclotrisilazane in one step. In addition, a mixture that was believed to contain both mono and bis derivatives was treated with potassium and trimethylchlorosilane in an attempt to increase the amount of the bis derivative to the point where it could be isolated. Only the reaction that started with pure N-trimethylsilylhexaphenylcyclotrisilazane successfully produced the pure bis derivative, and in that reaction the yield was only 6.3%.

a. From N-trimethylsilylhexaphenylcyclotrisilazane

The preceding report, page 5, described the preparation of N,N'-bis(trimethylsilyl)hexaphenylcyclotrisilazane by adding 1 mole of potassium to 1 mole of N-trimethylsilylhexaphenylcyclotrisilazane and treating the potassium derivative with trimethylchlorosilane. The yield of pure N,N'-bis(trimethylsilyl)hexaphenylcyclotrisilazane was only 6.3%. Identification has now been completed. The melting point was 226-227°C. The NMR spectrum, the molecular weight, and the elemental analysis confirmed the identity.

Found: C, 68.98%; H, 6.51%; N, 5.78%; Si, 19.1%

Calculated: C, 68.51%; H, 6.71%; N, 5.71%; Si, 19.07%

The molecular weight by vapor osmometry was 724 (average 728 and 720); theory 736.3. The determination was done by Galbraith Laboratories, Inc., Knoxville, Tennessee.

b. From hexaphenylcyclotrisilazane

The first attempt to attach two trimethylsilyl groups to hexaphenylcyclotrisilazane was described in the preceding report. A second attempt was made with styrene as suggested by Breed<sup>1</sup> for silylation of hexamethylcyclotrisilazane. In a 500-ml flask fitted with a magnetic stirrer, reflux condenser, and thermometer were placed 60 ml of dioxane, 2.8 g (0.0743 mole, 10% excess) of metallic potassium, 20.0 g (0.0338 mole) of hexaphenylcyclotrisilazane dissolved in 150 ml of purified dioxane, and 6.5 g (0.0676 mole) of freshly distilled styrene. The resulting solution was refluxed for 3 hours. At the end of this time all but a trace of the potassium had reacted. The solution was cooled, and 8.06 g (0.0743 mole, 10% excess) of trimethylchlorosilane in 15 ml of dioxane was added slowly. A white precipitate, presumably potassium chloride, formed during the following 2 hours of refluxing. The mixture was cooled, and the precipitate was filtered off. The residue, after being washed with dioxane and dried, weighed 5.4 g (theory for KCl, 5.54 g).

The product was distilled to remove the dioxane, and the undistilled portion was dissolved in Skellysolve B. Fractional crystallization yielded the following:

1. 1.6 g, mp 157-160°C
2. 2.1 g, mp 137-143°C
3. 16.0 g, viscous grease
- 19.7 g, total

The viscous grease was distilled at low pressure. The following fractions were obtained:

1. 6.3 g, bp 120-245°C at 0.1 mm, mobile liquid
2. 3.5 g, bp 265-285°C at 0.06 mm, viscous liquid
3. 5.3 g, viscous liquid residue, solid at room temperature
- 15.1 g, total

The residue was soluble in benzene. It will be examined for possible utility.



c. From a mixture of mono- and bis- trimethylsilyl derivatives

In previous preparations, two batches of impure products were obtained that were believed to be mixtures of mono- and bis- trimethylsilyl derivatives of hexaphenylcyclotrisilazane. It was thought that these might be further silylated by treating them with potassium and trimethylchlorosilane. NMR spectra were used to show how much additional reaction was required to convert the mixture entirely to the bis derivative. The attempt was not successful.

One batch of impure silyl derivatives, 1.8 g, was found to contain 62 mole % of the mono and 38 mole % of the bis derivative. The other, 3.7 g, was found to contain 56 mole % of the mono and 44 mole % of the bis derivative. Thus, in the total weight, 5.5 g, there was 4.6 millimoles of the mono derivative.

In a 300-ml, 3-neck flask fitted with magnetic stirrer, thermometer, and reflux condenser were placed 60 ml of purified dioxane, 0.196 g (0.005 mole, 10% excess) of metallic potassium, and 5.5 g of the mixture of mono and bis silyl derivatives in 100 ml of dioxane. The resulting solution was refluxed for 3 hours. At the end of this time all but a trace of the potassium had reacted. The solution was cooled, and 0.543 g (0.005 mole, 10% excess) of trimethylchlorosilane was added in 10 ml of dioxane. A white precipitate, presumably potassium chloride, formed during an additional 2 hours of refluxing. The mixture was cooled and centrifuged.

The clear solution was distilled to remove the dioxane, and the undistilled portion was dissolved in Skellysolve B. After extensive fractional crystallization, the following fractions were obtained:

1. 0.3 g, mp 171-171.5°C
2. 0.2 g, mp 167-168°C
3. 4.7 g, viscous grease
- 5.2 g, total

No fraction had a satisfactory melting point to indicate that it contained the desired product. The total amount recovered was 94.5% of the starting material.

d. Polymerization of N,N'-bis(trimethylsilyl)hexaphenylcyclotrisilazane

N,N'-bis(trimethylsilyl)hexaphenylcyclotrisilazane, 0.1011 g (0.14 millimole), was placed in an 8-mm test tube which was then swept with nitrogen. The open end was capped by crimping aluminum foil over the top, and the bottom was inserted into an oven through a hole in the door. The capped end was left outside of the oven. After 5 hours at 400°C, the material in the tube was a dark brown liquid, but it had become perceptibly more viscous. At the end of 13 hours at 400°C, the sample was solid. At the end of 23 hours at 400°C, no additional visible change had occurred. The solid, vitreous, brown product was not soluble in benzene; and it would not melt on a spatula at red heat. It was not foamed. In the 23 hours at 400°C, the sample lost 35% of its weight. The polymerization will be repeated to obtain a sample heated a shorter time.

2. N-(trimethylsilyl)hexamethylcyclotrisilazane

The N-trimethylsilyl derivative of hexamethylcyclotrisilazane was first prepared as described previously<sup>3</sup> by the method of Breed.<sup>1</sup> The potassium method that had been used successfully with hexaphenylcyclotrisilazane was tried for preparing additional quantities of the silyl derivative of hexamethylcyclotrisilazane for our future work. In the first attempt, the potassium would not dissolve in hexamethylcyclotrisilazane. Consequently, the reaction was started again, and styrene was added to promote the reaction of potassium. The procedure was as follows:

In a 2-liter, 3-neck flask fitted with a condenser, thermometer, magnetic stirrer, and dropping funnel were placed 27.2 g (0.124 mole) of hexamethylcyclotrisilazane, 600 ml of dioxane, and 5.0 g (0.128 mole) of potassium. To this mixture, 10.0 g (0.096 mole) of styrene in 6 ml of dioxane was added. After 2 hours of refluxing all but a trace of potassium had dissolved. Trimethylchlorosilane, 13.43 g (0.124 mole) in 50 ml of dioxane was added dropwise, and the mixture was refluxed for another 2 hours. The resulting mixture was cooled and centrifuged, and the clear solution was distilled to obtain 16.8 g (45.6% yield) of N-trimethylsilylhexamethylcyclotrisilazane,  $n_D^{25}$  1.4582. NMR spectra showed the correct ratio of methyl groups. A high-boiling viscous residue, 8.8 g, was also obtained. It will be examined further.

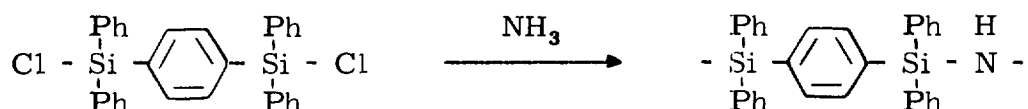
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3. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, April 29, 1963, pages 83-88.

### III. SILICON-NITROGEN POLYMERS CONTAINING AROMATIC BRIDGES

#### A. Discussion

Efforts were continued to prepare a highly aromatic polymer containing silicon-nitrogen units bridged by phenyl rings. The plan was to treat 1,4-bis(diphenylchlorosilyl)benzene with ammonia.



The method of Newing, Davis, and Towers<sup>4</sup> was used to prepare 1,4-bis(diphenylchlorosilyl)benzene. They did not isolate the pure compound, however; and that proved to be a very difficult task. Extensive tedious recrystallization with all of the containers in a nitrogen-filled bag finally produced a white crystalline product that on titration with standard base was found to have a neutral equivalent of 384 (theory, 256). Although the dichloro compound was not pure, it was thought that continued effort was achieving very little improvement, and so the compound was treated with ammonia. The resulting polymer was a waxy solid that bubbled when heated on a spatula. After a short heating time followed by cooling, it passed through a viscous stage where long fibers could be pulled from the melt with a glass rod. However, the fibers were brittle. Continued heating, up to red heat, converted the polymer to a friable mass. Thermal stability appeared to be much better on a panel. The polymer was spread on an aluminum panel and heated until smoking stopped. Unfortunately, the fused mass puddled and did not form a smooth coat. A mixture of 9 parts with 1 part of ethylenediamine silazane was heated on a panel for an hour at 500°C, and the resulting polymer was tough and flexible when cooled. Even in areas where it was 1-2 mils thick, although it could be torn, it did not crack off the panel when it was scratched with a sharp point. Elemental analysis supported the neutral equivalent in indicating that the polymer contained considerable oxygen. In view of the promising properties, attempts to prepare the pure 1,4-bis(diphenylchlorosilyl)benzene will be continued.

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4. C. W. Newing, Jr., F. C. Davis, and R. S. Towers (Stauffer Chemical Company), Quarterly Progress Report 5, Contract NAS 8-1510.

## B. Experimental Details

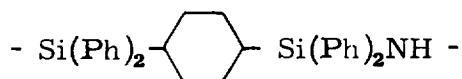
The attempt to prepare 1,4-bis(diphenylchlorosilyl)benzene was carried out as follows: In a 3-liter, 3-neck flask fitted with a stirrer, reflux condenser, thermometer, and dropping funnel were placed 29.2 g (1.2 mole) of magnesium turnings and 300 ml of tetrahydrofuran. To this was added dropwise, 141 g (0.6 mole) of p-dibromobenzene that had been dissolved in tetrahydrofuran. The resulting mixture was refluxed 2 hours and then left over the weekend in a nitrogen atmosphere. The solution of the Grignard Reagent was added over a period of 2 hours to 303 g (1.2 mole) of diphenyldichlorosilane in 500 ml of tetrahydrofuran. The mixture was stirred for 3 hours and left in a nitrogen atmosphere overnight. The tetrahydrofuran was removed by rapid distillation, and the residue was stirred with 1800 ml of heptane. The liquid suspension was filtered while all of the apparatus was in a polyethylene bag filled with nitrogen. The colorless filtrate was cooled in dry ice and then left overnight in a refrigerator, whereupon a few crystals formed. These were filtered in the dry bag and were found to have a neutral equivalent of 504 (theory, 256). Three successive recrystallizations reduced the neutral equivalent to 384. The product weighed 10.7 g (3.5% yield).

The crystalline product, presumably 1,4-bis(diphenylchlorosilyl)benzene, was treated with ammonia in the following manner: In a 1 liter, 3-neck flask fitted with stirrer, reflux condenser, thermometer, and gas inlet tube were placed 200 ml of benzene and 10.7 g (0.0209 mole) of crude 1,4-bis(diphenylchlorosilyl)benzene. Ammonia was passed through the gas inlet tube for 9 hours, and a positive pressure of ammonia was maintained on the reaction with the aid of a balloon on top of the condenser. The Beilstein Test for halogen was negative. The solution was refluxed for 3 hours. After being cooled, the reaction mixture was filtered to remove ammonium chloride. The benzene was distilled off; and the residue, 7.2 g, was a creamy, waxy solid. The elemental composition was:

Found: C, 73.61%; H, 5.34%; N, 2.39%; Si, 11.5%

Calculated: C, 79.07%; H, 5.53%; N, 3.07%; Si, 12.33%

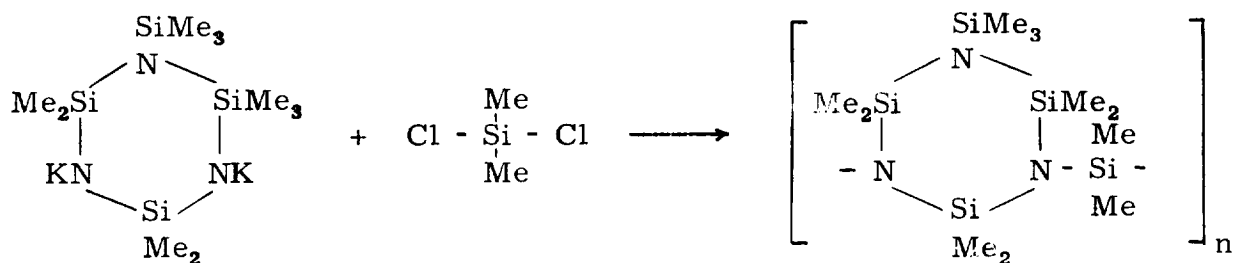
for the formula



#### IV. ANTICIPATED WORK

The study of polymers made from trimethylsilyl derivatives of hexamethylcyclotrisilazane and hexaphenylcyclotrisilazane will be continued. The mechanism of the thermal polymerization of the hexaphenyl derivatives will be investigated by analyzing the by-products and determining whether different mechanisms of polymerization occur at different temperatures. We will attempt to increase the amount of linear polymerization by choice of reaction conditions.

Polymerization of N-trimethylsilylhexamethylcyclotrisilazane will be attempted through the dipotassium derivative by reaction with dimethyl-dichlorosilane:



The Si-N polymer with phenylene bridges will be remade with additional efforts to protect the reactants from oxygen and moisture. The preceding efforts involved more lapsed time than necessary, and it may be possible to avoid side-reactions and contamination by shortening the time schedules during synthesis.

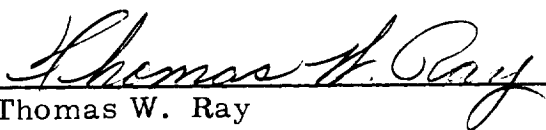
## V. TIME EXPENDITURE

The time expenditure during the current report period (May) was 593 man-hours.

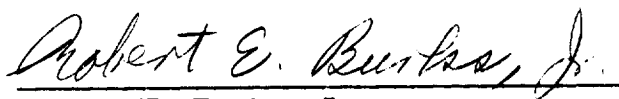
## ACKNOWLEDGMENTS

Mr. Robert E. Lacey, Senior Chemical Engineer, has assisted with the planning and interpretation of the laboratory work. Mssrs. William L. Mayfield, Charles L. Christy, Jr., Howard A. Kirk, and Franklin D. Alexander, Research Technicians, assisted with the laboratory work.

Submitted by:

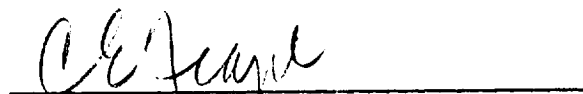


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Physical Sciences Division

Birmingham, Alabama  
June 14, 1963  
5948-1259-XXVIII  
(12:11:15) rc

# PROGRAM PLANNING CHART

	Allotted time, man-hours	1963												1964		
		April	May	June	July	August	September	October	November	December	January	February	March			
A. Synthesis of Polymers and Compounds with Desired Characteristics																
1. Lubricants - unsymmetrical derivatives of cyclic silazanes (see B. 1. b)	400			X												
2. Elastomers - silyl derivatives of ethylenediamine (see B. 7)	400				X											
3. Structural plastics	900	X	X	X	X											
B. Study of the Chemistry of Silicon-Nitrogen Compounds																
1. Metallation of silylamines as a method of synthesis	500	X	X	X												
a. Lubricants (see A. 1)	-															
b. Lubricants (see A. 1)	900						X	X	X	X	X					
c. Organometallics																
2. Polymerization of cyclic silazanes at high temperatures and pressures	280				X											
3. Condensation polymerization of silylamines with difunctional aromatic compounds	280															
4. Steric factors to inhibit cyclization	900							X	X							
5. Polyethylenimine as a source of silicon-nitrogen polymers	400			X				X	X	X	X					
6. Properties of methylhydrogen silazanes	200						X	X								
7. Elastomers from ethylenediamine silazanes (see A. 2)	-															
8. Addition of silicon tetrafluoride to silazanes and amines	280															
9. Heats of combustion as indicators of aromaticity	420			X	X	X			X							
10. Polymers from methyltrichlorosilane and silicon tetrachloride	510															
11. Silicon-nitrogen compounds with aromatic bridges	510	X	X	X						X	X					
12. Factors affecting hydrolytic and thermal stabilities	510			continuous												
C. Evaluation of Polymers (thermal, hydrolytic, and radiation stability)	510			continuous												
D. Applications - Search for New Uses	510			continuous												
E. Heat Barriers	510			At time designated by NASA												
F. Preparation of Final Report	170															
	9000															X

Descriptions correspond to sections of Proposal 2186 - March 20, 1963.

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